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Silicon vacancy in SiC: A high-spin state defect

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We report results from spin-polarized *ab initio* local spin-density calculations for the silicon vacancy (V_{Si}) in 3C– and 2H–SiC in all its possible charge states. The calculated electronic structure for SiC reveals the presence of a stable spin-aligned electron-state t_2 near the midgap. The neutral and doubly negative charge states of V_{Si} in 3C–SiC are stabilized in a high-spin configuration with $S=1$ giving rise to a ground state, which is a many-electron orbital singlet $^3T_1$. For the singly negative V_{Si}, we find a high-spin ground-state $^4A_2$ with $S=3/2$. In the high-spin configuration, V_{Si} preserves the T_d symmetry. These results indicate that in neutral, singly, and doubly negative charge states a strong exchange coupling, which prefers parallel electron spins, overcomes the Jahn–Teller energy. In other charge states, the ground state of V_{Si} has a low-spin configuration. © *1999 American Institute of Physics.* [S0003-6951(99)04702-6]

The electronic structure of a vacancy in a covalent solid can be simply discussed using a one-electron orbital model (linear combination of atomic orbitals).[1] Even though the ground state of the vacancy in silicon can be qualitatively described within a single-electron picture,[2] it is found in some wide-band-gap semiconductors, such as diamond and GaP,[3,4] that finally, many-electron effects determine the electronic properties of the vacancy. According to the one-electron model, the defect molecular orbitals are an a_1 singlet and a t_2 triplet. By distributing the electrons over the orbitals, one can determine the ground state as the configuration with the lowest total energy.[1] Coulson and Larkins[5] predicted a high-spin ground-state $^4A_2(a_1^2t_2^3)$ for the vacancy V_C^{1-} in diamond, which is not subject to Jahn–Teller distortion. The many-electron singlet $^4A_2$ is stabilized by a strong exchange coupling (spin–spin interaction), which is larger than the corresponding Jahn–Teller energy. For the vacancy in diamond, the $^4A_2$ state has been confirmed experimentally.[3] A similar high-spin ground state is also found for the neutral vacancy V_{Ga}^0 in GaP.[4] Like diamond and GaP, silicon carbide is a wide-band-gap material. Several observations obtained from electron-spin-resonance (ESR), optically detected magnetic-resonance (ODMR), photoluminescence (PL), and electron-nuclear double-resonance (ENDOR) measurements assigned to silicon vacancy-related centers, high-spin states $S=1$ and $S=3/2$ have been reported.[6–9] Recently, an all-electron linear muffin-tin orbital ASA calculation for unrelaxed V_{Si}^{1-} in SiC has been carried out,[10] in which a large energy separation between the low-spin ($S=1/2$) and the high-spin ($S=3/2$) configurations was obtained.

In this letter, we present the *ab initio* characterization of the silicon vacancy in SiC in all stable charge states. Fully relaxed vacancies are studied both in cubic (3C–SiC) and hexagonal (2H–SiC) silicon carbide. We have used the plane-wave pseudopotential method (PWPP), where the exchange-correlation functional of the many-body electron–electron interaction is described within the local-density (LDA)[10] or local-spin-density (LSD) approximation.[11] All the calculations are performed using a large 128 atom supercell. For the detailed description of the standard formalism concerning the charged supercell calculations, see Ref. 12. Further computational details can be found in Refs. 13–17. We use experimental band-gap values in the formation energy analysis because of the well-known fact that the gap calculated from the single-particle Kohn–Sham states underestimates severely the true band gap. The experimental band gap for 3C–SiC is 2.39 eV, while the obtained LDA gap is 1.30 eV.

We find that the silicon vacancy in 3C–SiC has stable charge states from $2+$ to $4-$. In Fig. 1, the formation energies of different charge states as a function of the electron chemical potential are shown for C-rich SiC. For neutral V_{Si}, the formation energy is relatively high, ~7.1 eV in C-rich conditions. However, due to the large band gap of SiC, the formation energy varies strongly with the electron chemical potential. The ionization levels found for 3C–SiC are listed in Table I. We find the singly negative vacancy to be the stablest charge state in the range from 0.5 to 1.2 eV of the electron chemical potential. The doubly positive vacancy is stable up to the value of 0.4 eV of the electron chemical potential. The doubly negative vacancy is stable in ~130 meV wide range, while the $1+$, neutral, and $3-$ states are found to be only marginally stable defects in very narrow windows of chemical potential. It is possible that negative-U transitions take place between the states $(2+/0)$ and $(2$

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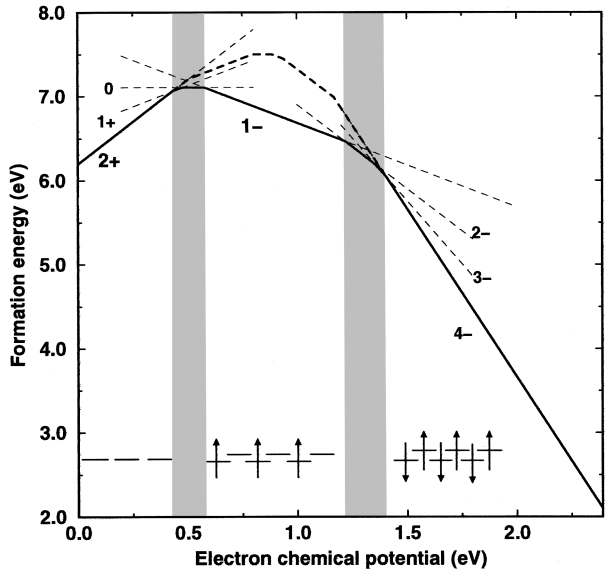

FIG. 1. Formation energy of the silicon vacancy in 3C–SiC grown under C-rich conditions. The vertical axis shows the formation energy and the horizontal axis the electron chemical potential. There are two deep levels at 0.5 eV above the valence-band maximum. The rest of the states are about 1.3 eV above the valence-band maximum. The significance of the exchange to the formation energy can be seen in the mid-band-gap region, where the results of the high-spin LSD calculations are shown as the lower solid line and results from the spin-compensated calculation as the dotted line.

$-/4-$). Still, because of the restricted accuracy of the density functional theory (DFT) LSD method, one cannot confirm whether for narrow ranges of the electron chemical potential the charge states $1+$ and $3-$ stabilize as well. Moreover, it is not determined whether the charge state $4-$ actually exists, because the ionization level of V_{Si}^{4-} is located above the LDA band-gap edge.

Figure 1 illustrates the three governing occupations of the one-electron-state t_2 triplet: empty (V_{Si}^{2+}), triply occupied by spin-aligned electrons (V_{Si}^{1-}), and fully occupied (V_{Si}^{4-}). At the two borderlines of these three zones (the grey regions in Fig. 1) we find two stable charge states V_{Si}^{0} and V_{Si}^{2-} with spin $S=1$. The parallel spin occupation of t_2 with $S=1$ corresponds the ground state of the many-electron orbital state ${}^3T_1$.[1,5] The spin-aligned $(t_2)^3$ ground state with $S=3/2$ stands for the orbitally degenerate singlet ${}^4A_2$.[1,5] The exchange energies are most pronounced in the mid-band-gap region (see Fig. 1). The effect of the spin polarization in the formation energies in different charge states is listed in Table II. In 3C–SiC, the $1-$ charge state with spin $S=3/2$ has the strongest effect of the spin polarization $\sim$0.58 eV. For the high-spin states $S=1$ of V_{Si}^{0} and V_{Si}^{2-} defects, we find the exchange energy gain in the spin-polarized calculation as large as 0.4 eV. For the $S=1/2$ configurations of V_{Si}^{1+} and V_{Si}^{3-}, the gain is remarkably less. Obviously, in the spin-compensated regions with spin $S=0$, corresponding to the charge states V_{Si}^{2+} and V_{Si}^{4-}, the LDA and LSD results coincide (see Fig. 1).

TABLE I. Ionization levels for the relaxed Si vacancy in 3C– and 2H–SiC from LSD calculations (in eV above the valence-band maximum).

	2+/1+	1+/0	0/1−	1−/2−	2−/3−	3−/4−
3C	0.433	0.495	0.561	1.224	1.353	1.403
2H	0.047	0.133	0.317	0.908	1.044	1.242

TABLE II. The effect of spin polarization in 3C– and 2H–SiC in different charge states of the silicon vacancy. $\Delta E=|E^{\mathrm{LSD}}-E^{\mathrm{LDA}}|$ is evaluated from the energy difference between the spin-compensated (LDA) and the spin-polarized (LSD) calculation in electron volts (eV). In the LDA result (E^{LDA}), the spin state is always low: either $S=0$ or $S=1/2$, whereas in the LSD result (E^{LSD}) the total spin in each charge state corresponds to the ground-state spin configuration and is marked in the second line of Table II.

	1+	0	1−	2−	3−
	$S=\frac{1}{2}$	$S=1$	$S=\frac{3}{2}$	$S=1$	$S=\frac{1}{2}$
3C	0.076	0.378	0.580	0.419	0.241
2H	0.143	0.317	0.458	0.183	0.090

In cubic SiC, the four carbon atoms surrounding V_{Si}, forming thus a tetrahedron, stretch their mutual distances, depending on the charge state, by 8%–14% compared to the C–C distance of 3.044 Å in the ideal SiC crystal. This distance tends to get shorter when electrons are added to the system. Characteristic for the high-spin state ($S=3/2$) and for the $2+$ and $1+$ charge states is a symmetric T_d relaxation. A small symmetry breaking is found when the charge increases: other charge states are weakly Jahn–Teller distorted. The volume increase of the tetrahedron, formed by the C atoms surrounding the Si vacancy, compared to the ideal case in 3C–SiC, is 30%–47%, depending on the charge state.

The most common SiC polytypes (4H and 6H–SiC) are composed of two inequivalent lattice sites, cubic and hexagonal. Our extensive study for 3C–SiC outlines the characteristics of the cubic-site vacancy. Although the local atomic surroundings of the cubic and hexagonal vacancies do not considerably differ from each other, the electronic structure can be altered substantially. In order to understand the qualitative difference between the two lattice sites, we also performed a study of the hexagonal-site vacancy in 2H–SiC.[14]

In 2H–SiC, the formation energy of the silicon vacancy is found to be 7.8 eV in C-rich conditions, i.e., slightly higher than in 3C–SiC. Like 3C–SiC, in 2H–SiC the vacancy stabilizes in the high-spin configuration in neutral, singly, and doubly negative charge states. In 2H–SiC, the effect of spin polarization is qualitatively the same as for 3C–SiC (see Table II). The ionization levels for V_{Si} in 2H–SiC are listed in Table I. Compared to 3C–SiC, the ionization levels are located lower in the band gap by 0.16–0.39 eV, depending on the charge state. The $1+$, neutral, and $3-$ charge states are found to be stable in a much wider range of electron chemical potential in 2H–SiC than in 3C–SiC. The negative-U behavior is not found for 2H–SiC. The C atoms surrounding V_{Si} stretch their mutual distances by 8%–12% compared to the ideal 2H–SiC crystal. Like 3C–SiC, in the high-spin configuration ($S=3/2$) and $2+$ charge state, the defect maintains the T_d symmetry, but in the case of V_{Si}^{1+} the Jahn–Teller distortion is noticed in 2H–SiC. The rest of the charge states are weakly Jahn–Teller distorted.

According to the experimental work,[6,7,9,18] the silicon vacancy in SiC is negatively charged, exhibits T_d symmetry and is most often assigned to be V_{Si}^{1-}. For V_{Si}-related centers, signals both from a high-spin configuration $S=3/2$ (Ref. 9) and from a low-spin $S=1/2$ (Refs. 6 and 18) are observed.

Our calculations indicate that the experimentally detected signal with $S=3/2$ arises from the singly negative V_{Si} and thus confirms the result of Wimbauer *et al.*[9] Our results further suggest that the signals in 3C–SiC with $S=1/2$ (Refs. 6 and 18) could be explained by V_{Si}^{1+} or V_{Si}^{3-}.

In the case of the vacancy in diamond and GaP, the high-spin ground state appears only for the charge state, where the gap state is the spin-aligned $(t_2)^3$. For 3C–SiC, the $(t_2)^3$ corresponds to the singly negative charge state. As a particular character of 3C–SiC, we find the spin-paired neutral and doubly negative charge states, corresponding to occupations $(t_2)^2$ and $(t_2)^4$, stabilize in the high-spin configuration with $S=1$ as well.

In summary, we characterize the silicon vacancy in cubic and hexagonal sites in SiC using the LSD approximation. In 3C– and 2H–SiC, for neutral, singly, and doubly negative charge states the exchange coupling overcomes Jahn–Teller energies, and the silicon vacancy is found in the high-spin ground state with T_d symmetry. In the high-spin configuration the V_{Si} maintains the T_d symmetry. A weak Jahn–Teller effect occurs in the low-spin configuration. Our finding of the high-spin ground state agrees with recent experiments,[9] and can sort out several open questions related to the silicon vacancy in SiC.[6–8,18] Our result also offers a resolution to the ambiguity, why, in SiC, are both high-spin and low-spin signals observed for V_{Si}.

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